Mixed bismuth oxides with layer lattices

II. Structure of $Bi_4Ti_3O_{12}$

By BENGT AURIVILLIUS

With 5 figures in the text

By means of X ray analysis it has been found that the crystal structures of a number of bismuth oxyhalides consist of $Bi_2O_2^{2+}$ layers alternating with layers of halogen ions (1, 2). In all these cases the symmetry was found to be tetragonal and the lengths of the a axes almost constant ≈ 3.8 Å.

On making an X ray study of the system Bi_2O_3—TiO_2 a phase (of composition about 40 atomic % TiO_2) was found, the powder photographs of which could be explained by assuming a pseudo-tetragonal cell with $a = 3.84$ and $c = 32.8$ Å. It seemed of interest to make a closer study of this phase since the cell dimensions and composition seemed to indicate a layer lattice with $Bi_2O_2^{2+}$ layers, but of a type hitherto uninvestigated.

Procedure: Weighed amounts of Bi_2O_3 (puriss) and TiO_2 (puriss) were mixed and heated to about 1100° C for some hours in a weighed platinum crucible. After cooling the crucible was weighed again and the composition calculated by assuming that the loss of weight could be ascribed to the volatility of Bi_2O_3. Powder photographs of various preparations in the system Bi_2O_3—TiO_2 indicated that there is a phase with a body-centered pseudo-tetragonal unit cell with $a = 3.841$ and $c = 32.83$ Å at compositions about 40 mole % TiO_2. It was, however, impossible to get samples which were quite free from impurities so the powder photographs always contained a few extra lines.

The lines $21l$, $22l$ and $31l$ were found to be split up. No cleavage was, however, found for the lines $10l$, $20l$ and $30l$. This could be explained by assuming a face-centered orthorhombic unit cell with the same c axis as the pseudo-tetragonal cell and with its a and b axes equal to the diagonals $(a\sqrt{2})$ of the pseudo cell.

The orthorhombic axes will be: $a = 5.410$　$b = 5.448$　$c = 32.84$ Å. The observed density (40 mole % TiO_2) is 7.85. If the composition is assumed to be $Bi_4Ti_3O_{12}$ (43 mole % TiO_2) and 4 formula units are assumed per unit cell the calculated density will be 8.04 which agrees fairly well with the observed value.

Single crystals, thin plates, were picked out and Weissenberg photographs (zero layer and first layer) were taken around the 3.84 axes, thus registering $h0l$ and $h1l$ (pseudo cell) or hhl and $h, h + 2, l$ (orthorhombic cell).

499

B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

Though there was nothing in the Weissenberg photographs to indicate lower Laue symmetry than $D_{4h} - 4/mmm$, it was — as has already been mentioned — found from the powder photographs that the real symmetry was not higher than orthorhombic (Laue symmetry $D_{2h} - mmm$).

Except for the extinctions following from the face-centering (hkl occurring only for h, k, l all odd or even) no systematic extinctions were found, which is characteristic of the space groups C_{2v}^{18}, D_2^7 and D_{2h}^{23}.

Positions of the bismuth atoms

Since the intensities of hkl with h, k, l all odd on one side and the intensities of hkl with h, k, l all even on the other side appeared to vary in the same way with l (see Table 1), it seemed probable that at least the bismuth atoms are situated on the lines: $(000; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}) + 00z$. The sum of

$$\sum_l I_{001} \cos 2\pi l z \quad \text{and} \quad \sum_l I_{111} \cos 2\pi l z$$

will under such conditions represent the Patterson function along $00z$. These two sums are pictured in figure 1. It is seen from the graph that high maxima occur at $z = 0.144$, 0.280 and 0.428. If $C_{2v}^{18}c$ is not considered, only the following positions on the lines $00z$

Table 1

Weissenberg Photographs of $Bi_4Ti_3O_{12}$. Cu K_α radiation

l	Icalc.	Iobs.				l	Icalc.	Iobs.		
		0 0	2 0 or 0 2	2 2	4 2 or 2 4			1 1	3 1 or 1 3	3 3
2	4.4		—	vvw	—	1	130	vst	m	m
4	20		w	w	—	3	14	w	—	—
6	85	m	m	m	w	5	18	m⁻	vvw	—
8	180	m	m	m	w⁺	7	390	vst	m⁺	m⁺
10	8.4	w	m⁻	vvw	—	9	0.01	—	—	—
12	42	m	m⁻	w	—	11	26	w	vw	vw
14	360	vst	m	m	m	13	42	w	vw	vw
16	3.6	m⁺	—	vvw	—	15	230	w	vw	—
18	32	m	w	vvw	—	17	4.4	—	—	—
20	12	m⁻	w	—	—	19	74	m	vvw	vw
22	260	st	st	m	m	21	300	st	m	w
24	2.0	w	w	vw	—	23	14	m	w	vw
26	110	m	st	st	m⁺	25	37	m	m	w
28	240	m	st	st	st	27	0.09	—	—	—
30	27	w	m	m⁻	m	29	280	st	st	st
32	40	m⁻	st	m	st	31	0.6	w	w	—
34	7.8	vw	w	vw		33	150	st	st	st
36	280	m	vst	vst		35	170	st	st	
38	0.1	vw	w	vw		37	41	m	m	
40	190	m	vst			39	40	st		
42	110	m				41	36	m		

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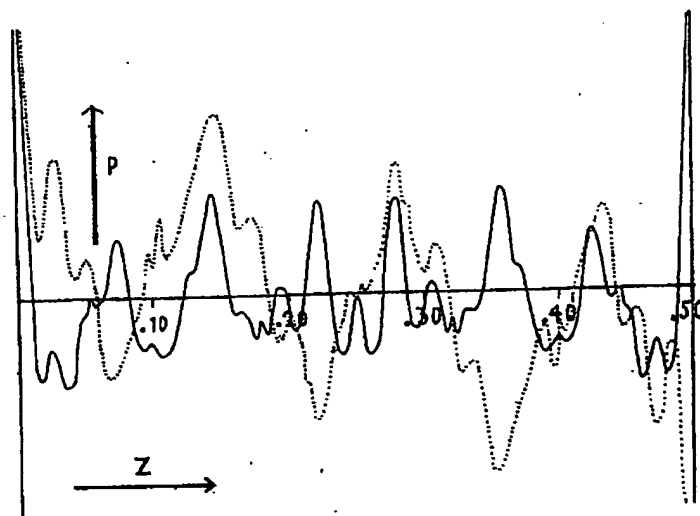
Figure 1. Patterson function of $Bi_4Ti_3O_{12}$ along $0\,0\,z$

Full curve: $\sum_l I_{00l} \cos 2\pi l z$

Dotted curve: $\sum_l I_{11l} \cos 2\pi l z$ (orthorhombic indices)

are possible for the Bi atoms: The two 4-fold positions $0\,0\,0$ and $0\,0\,\frac{1}{2}$ and the 8-fold positions $\pm\,0\,0\,z$. Assuming that the unit cell contains 16 Bi it was found that the observed maxima in the graph could be explained by assuming that the 16 Bi atoms are situated in two 8-fold positions $\pm\,0\,0\,z$. In this way three possibilities arose:

a. $z_1 = 0.215$ $z_2 = 0.356$

b. $z_1 = 0.072$ $z_2 = 0.356$

c. $z_1 = 0.072$ $z_2 = 0.215$.

If the influence of the Ti and the O atoms is neglected the Patterson maxima will have the following relative weights:

	a	b	c
0.144	2	1	3
0.280	1	3	2
0.428	3	2	1

If the two curves in figure 1 are added and the areas under the peaks calculated, the ratio of (0.144) : (0.280) : (0.428) is found to be: 4.4 : 2.6 : 1.0. Now, these figures cannot be directly compared with the figures given above, since the zero level in the graph is unknown. It is, however, seen that the observed order of magnitude of the peaks (0.144) (0.280) and (0.428) is the same as

B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

that calculated for c. Case c was therefore assumed, and z_1 and z_2 were varied around 0.072 and 0.215. The observed intensities were found to agree quite well with those calculated for $z_1 = 0.067 \pm 0.004$ and $z_2 = 0.211 \pm 0.004$. In Table 1 the observed intensities are compared with intensities calculated as follows: $I = A^2$ $A = 10 \cdot (\cos 2\pi l z_1 + \cos 2\pi l z_2) = 10 F/4 f_{Bi}$. In Table 1 the lines of maximum absorption (see (4)) are indicated by dotted lines. If allowance is made for the polarisation factors and the absorption effect (4) it is seen that for h, k, l all odd the observed and calculated intensities agree quite well. For h, k, l all even the calculated ratios of $0016:0018$ and $2216:2218$ are inversed in comparison with the observed ratios. This might be due to the influence of the Ti and the O atoms.

Positions of the Ti atoms

With the formula assumed the unit cell contains 12 Ti atoms. If the space group $C_{2v}^{18} c$ is not considered, the only 4-fold positions possible are:

4 (a) $x\,0\,0$ or $0\,y\,0$ ($C_{2v}^{18} a$ or b), 4 (a) $0\,0\,0$ 4 (b) $0\,0\frac{1}{2}$ (D_2^7, D_{2h}^{23}),

4 (c) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ 4 (d) $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ (D_2^7)

The positions $0\,0\,0$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ seemed very improbable since the distance Bi—Ti would then be only 2.2—2.4 Å. For the remaining positions $0\,0\frac{1}{2}$, $x\,0\,0$ (or $0\,y\,0$) x (or y) must lie within the limits 0.38—0.62, if the minimum distance Bi—Ti is assumed to be 3.0 Å. If the distance Ti—Ti is assumed to be ≥ 3.0 Å, only 4 Ti can be situated in 4-fold positions and the remaining 8 Ti must occupy one 8-fold position. Of 8-fold positions the following seemed to be possible:

8 (d) $x\,0\,z$, $x\,0\,\bar{z}$ (or $0\,y\,z$, $0\,y\,\bar{z}$) $C_{2v}^{18} a$ or b, 8 (g) $\pm 0\,0\,z$ (D_2^7, D_{2h}^{23}),

8 (h) $\frac{1}{4}\frac{1}{4}z$, $\frac{1}{4}\frac{1}{4}\frac{1}{2} - z$ (D_2^7)

Thus there seemed to be two ways of arranging the Ti atoms:

1. 4 Ti$_1$ in $0\,0\frac{1}{2}$, 8 Ti$_2$ in $\frac{1}{4}\frac{1}{4}z$, $\frac{1}{4}\frac{1}{4}\frac{1}{2} - z$ $0.133 \leq z \leq 0.147$

2. 4 Ti$_1$ in $0\,0\frac{1}{2}$, $x\,0\,0$ (or $0\,y\,0$) $0.38 \leq x \leq 0.62$ (or $0.32 \leq y \leq 0.68$)

    8 Ti$_2$ in $\pm 0\,0\,z$ $0.324 \leq z \leq 0.398$, $x\,0\,z$, $x\,0\,\bar{z}$ (or $0\,y\,z$, $0\,y\,\bar{z}$)

    $0.38 \leq x \leq 0.62$ (or $0.38 < y < 0.62$) $0.102 \leq z \leq 0.176$

Both for 1 and 2 the parameters are chosen as to make the distances Bi—Ti ≥ 3.0 Å. The region possible for the Ti$_2$ atoms — assuming arrangement 2 — is shown by the shaded area in figure 2.

By calculating the intensities of $00l$ for various z_{Ti} values, it was found that the calculated ratio $0016:0018$ (see the discussion on the Bi positions) was best for $z \sim 0.13_0$ or 0.37_0.

The intensities of the spots in the Weissenberg photographs were then calculated for the arrangements 1 and 2 but no decision between 1 and 2 could be made by comparison with the observed intensities. It was therefore tried to find possible arrangements for the O atoms with both 1 and 2.

Case 1

Space group D_2^7 and the following positions for the metal atoms were assumed:

$$8 \text{ Bi}_1 \text{ in } 8 \text{ (g) } z_1 = 0.067 \pm 0.004 \quad 8 \text{ Bi}_2 \text{ in } 8 \text{ (g) } z_2 = 0.211 \pm 0.004$$

$$4 \text{ Ti}_1 \text{ in } 4 \text{ (b) } 00\tfrac{1}{2} \quad 8 \text{ Ti}_2 \text{ in } 8 \text{ (h) } 0.133 \leq z \leq 0.147$$
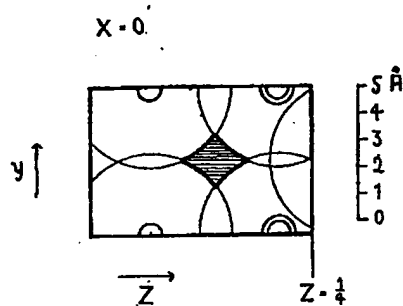
Figure 2.

By assuming that the distances $\text{Bi}-\text{O} \geq 2.2$, $\text{Ti}-\text{O} \geq 1.8$ and $\text{O}-\text{O} \geq 2.5$ Å, the following positions were found possible for the O atoms:

$$4 \text{ (a) } 000 \quad\quad 4 \text{ (c) } \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4} \quad\quad 4 \text{ (d) } \tfrac{1}{4}\tfrac{1}{4}\tfrac{3}{4}$$

$$8 \text{ (g) } \pm 00z \quad\quad\quad 8 \text{ (h) } \tfrac{1}{4}\tfrac{1}{4}z; \ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{2}-z$$

$$0.130 \leq z \leq 0.148 \quad\quad\quad 0 \leq |z| \leq 0.040$$

$$0.274 \leq z \leq 0.445 \quad\quad\quad -0.183 \leq z \leq -0.095$$

$$16 \text{ (k) } xyz; \ \bar{x}\bar{y}z; \ x\bar{y}\bar{z}; \ \bar{x}y\bar{z}$$

$$\begin{array}{cc} x \approx 0 & y \approx 0 \\ & \text{or} \\ y = 0.27 & x = 0.27 \end{array}$$

Two regions are possible:

$$z = 0.113 \text{ (for } z_{\text{Ti}} = 0.147) \text{ and } z = 0.165 \text{ (for } z_{\text{Ti}} = 0.132)$$

No combinations of these positions could be found giving reasonable distances and octahedra around the Ti atoms, as is the case in previously investigated structures containing Ti^{4+} and O^{2-}. Arrangement 1 seemed therefore improbable.

B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

Case 2

The positions of the metal atoms are assumed to be:

$8\ Bi_1$ in $\pm\ 0\,0\,z_1$ $z_1 = 0.067 \pm 0.004$ $8\ Bi_2$ in $\pm\ 0\,0\,z_2$ $z_2 = 0.211 \pm 0.004$

$4\ Ti_1$ in $0\,0\,\frac{1}{2}$, $x\,0\,0$ (or $0\,y\,0$) $0.38 \leq x, y \leq 0.62$ $8\ Ti_2$ in $\pm\ 0\,0\,z$,
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 0.324 \leq z \leq 0.398$

$x\,0\,z$; $x\,0\,\bar{z}$ (or $0\,y\,z$; $0\,y\,\bar{z}$) $0.38 \leq x, y \leq 0.62$
$\qquad\qquad\qquad\qquad\qquad 0.102 \leq z \leq 0.176$

At first only space group D_4^7 was considered (Ti_1 in $0\,0\,\frac{1}{2}$ and Ti_2 in $\pm\ 0\,0\,z$). The following positions were found possible for the O atoms making the same assumptions as in case 1:

4 (a) $0\,0\,0$ 4 (c) $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$

4 (d) $\frac{1}{4}\,\frac{1}{4}\,\frac{3}{4}$ 8 (g) $\pm\ 0\,0\,z$ 8 (h) $\frac{1}{4}\,\frac{1}{4}\,z$; $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{2} - z$
$\qquad\qquad\qquad\qquad 0.130 \leq z \leq 0.148$ $0 < |z| < 0.040$
$\qquad\qquad\qquad\qquad 0.379 \leq z \leq 0.445$ $0.095 < |z| < 0.183$
$\qquad\qquad\qquad\qquad 0.274 \leq z \leq 0.343$

16 (k) $x\,y\,z$; $\bar{x}\,\bar{y}\,z$; $x\,\bar{y}\,\bar{z}$; $\bar{x}\,y\,\bar{z}$
$\qquad x = 0.25 \pm 0.02 \quad y = 0.25 \pm 0.02$
$\qquad\qquad\qquad\qquad \text{or}$
$\qquad y \sim 0 \qquad\qquad x \sim 0$
$\qquad\qquad 0.114 < z < 0.163$

It was tried to find positions for the O atoms so that Ti_1 and Ti_2 would be surrounded by regular or almost regular octahedra of O atoms with distances $1.8 \leq Ti - 0 \leq 2.5$ Å. For O atoms in contact with Ti_1, the following point positions are possible: 8 (h) $0 < |z| < 0.040$, 8 (g) $0.424 \leq z \leq 0.445$. With 8 O situated at $\frac{1}{4}\,\frac{1}{4}\,0$; $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{2}$ and 8 O at $\pm\ 0\,0\ 0.442$ regular octahedra of O would surround Ti_1. It, therefore, seemed probable that oxygen atoms are situated near these positions.

For oxygen atoms in contact with Ti_2, the following positions are possible:

8 (g$_1$) $0.379 \leq z_1 \leq 0.445$ 8 (h) $0.095 \leq |z| \leq 0.183$

8 (g$_2$) $0.274 \leq z_2 \leq 0.343$ 16 (k) $0.114 \leq z \leq 0.163$

With one set of oxygen atoms situated at 8 (h) or 16 (k), every Ti_2 atom will be in contact with two oxygen atoms, while if oxygen atoms are situated at 8 (g$_1$) or 8 (g$_2$), Ti_2 will be in contact with only one oxygen atom. It was

504

found that only one set of oxygen atoms could occupy the positions 16 (k), 8 (g_1) and 8 (g_2), while at most 32 oxygen atoms could be situated in positions 8 (h). The following arrangements allowing Ti_2 to be in contact with 6 O are possible:

a. 16 O (k) + 8 O (h) + 8 O (h)

b. 16 O (k) + 8 O (g_1) + 8 O (g_2) + 8 (h)

c.   8 O (h) + 8 O (h) + 8 O (h)

d.   8 O (h) + 8 O (h) + 8 O (g_1) + 8 O (g_2)

With a and b no combination of positions could be found, giving octahedra of oxygen atoms around Ti_2.

c. With 8 O in $\frac{1}{4}\frac{1}{4}0$; $\frac{1}{4}\frac{1}{4}\frac{1}{2}$, 8 O in 0 0 0.442 and 24 O in positions 8 (h) ($z_1 \approx 0.102$ $z_2 \approx -0.139$ $z_3 \approx 0.177$) so as to form octahedra of oxygen atoms around Ti_1 and Ti_2, there was room for the remaining 8 O atoms only in the position $\pm 0\,0\,z$ $z = 0.274$ or in the positions 4 (c) + 4 (d). With these arrangements, however, the distances O — O would be short (≈ 2.4 Å).

With d, positions for the oxygen atoms could be chosen, allowing reasonable distances and giving octahedra of oxygen atoms around Ti_2. Arrangement d was, therefore, preferred to the arrangements a, b and c.

The following parameters were assumed for oxygen atoms in contact with Ti_1 or Ti_2:

$$8\ O_1\ \text{in } 8\ (h)\ z = 0$$
$$8\ O_4\ \text{in } 8\ (g)\ z = 0.436$$
$$(z_{Ti_2} = 0.372)\qquad 8\ O_5\ \text{in } 8\ (g)\ z = 0.308$$
$$8\ O_6\ \text{in } 8\ (h)\ z = 0.128$$
$$8\ O_7\ \text{in } 8\ (h)\ z = -0.128$$

Even if these parameters are varied considerably around the values given, room for the remaining 8 O is left only in the positions 4 (c) and 4 (d) (O_2, O_3).

The positions arrived at might also be described with space group D_{2h}^{23}—$F\,m\,m\,m$ as follows:

$$8\ O_1\ \text{in}\ \ 8\ (e)\ \tfrac{1}{4}\tfrac{1}{4}0;\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{2}$$
$$8\ O_2\ \text{in}\ \ 8\ (f)\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4},\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{3}{4}$$
$$8\ O_3\ \text{in}\ \ 8\ (i)\ \pm 0\,0\,z\ \ z = 0.436$$
$$8\ O_4\ \text{in}\ \ 8\ (i)\ \pm 0\,0\,z\ \ z = 0.308$$
$$16\ O_5\ \text{in}\ 16\ (j)\ \tfrac{1}{4}\tfrac{1}{4}z;\ \tfrac{1}{4}\tfrac{1}{4}\bar{z};$$
$$\tfrac{1}{4}\tfrac{1}{4}z;\ \tfrac{1}{4}\tfrac{1}{4}\bar{z}$$
$$z = 0.128$$

B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

The distances and coordination will be:

$Bi_1 - 4\ O_1 = 2.92$	$Ti_2 - \quad O_3 = 2.10$	$Ti_1 - 4\ O_1 = 1.92$
$Bi_1 - 4\ O_3 = 2.72$	$Ti_2 - \quad O_4 = 2.10$	$Ti_1 - 2\ O_3 = 2.10$
$Bi_1 - 4\ O_5 = 2.76$	$Ti_2 - 4\ O_5 = 1.92$	
$Bi_2 - 4\ O_2 = 2.79$	$O_1 - 4\ O_1 = 2.71$	
$Bi_2 - 4\ O_4 = 2.79$	$O_3 - 4\ O_1 = 2.83$	
$Bi_2 - 4\ O_5 = 2.29$	$O_4 - 4\ O_2 = 2.70$	
	$O_4 - 4\ O_5 = 2.83$	
	$O_5 - 4\ O_5 = 2.71$	

No new combinations were found if the space group D_{2h}^{23} was assumed instead of D_2^7.
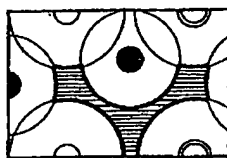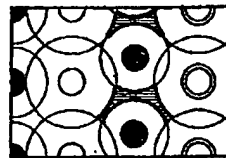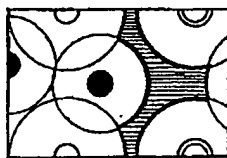

X = 0   X = $\frac{1}{4}$

Figure 3 a.

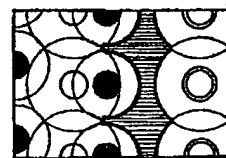X = 0   X = $\frac{1}{4}$

Figure 3 b.

Since $a \approx b$ and the positions of the O atoms must be chosen from space considerations, it does not matter whether space group C_{2v}^{18} *a* or *b* is assumed. C_{2v}^{18} *b* was assumed arbitrarily. It was found that oxygen atoms could only be situated in the planes $x = 0$, $x = 0.25 \pm 0.02$, $x = \frac{1}{2}$ and $x = 0.75 \pm 0.02$. Thus the following positions are possible:

$$4\ (a)\ 0\,y\,0 \qquad 8\ (b)\ \tfrac{1}{4}\,y\,\tfrac{1}{4};\ \tfrac{1}{4}\,y\,\tfrac{3}{4} \qquad 8\ (c)\ 0\,y\,z;\ 0\,y\,\bar{z}$$

$$8\ (d)\ x\,y\,0;\ \bar{x}\,y\,0 \qquad\qquad 16\ (e)\ x\,y\,z;\ \bar{x}\,y\,\bar{z};\ \bar{x}\,y\,z;\ x\,y\,\bar{z}$$

$$x = 0.25 \pm 0.02 \qquad\qquad x = 0.25 \pm 0.02$$

Table 2

Weissenberg Photographs of $Bi_4Ti_3O_{12}$. Cu K_α radiation

Zero Layer

0 0 l	$I_{calc.}$	$I_{obs.}$	2 0 l	$I_{calc.}$	$I_{obs.}$
6	56	m	2	1.0	vvw
8	61	m	4	12	w
10	12	w	6	59	m
12	58	m	8	81	m
14	450	vst	10	12	vvw
16	88	m+	12	55	w
18	30	m	14	440	m
20	19	m-	16	64	vvw
22	200	st	18	31	vvw
24	27	w	20	19	—
26	120	m	22	200	m
28	230	m	24	26	vw
30	62	w-	26	120	st
32	140	m-	28	230	st
34	4.0	vvw	30	62	m-
36	300	m	32	120	m
38	9.0	vw	34	4.0	vvw
40	110	m	36	290	vst
42	93	m	38	8.0	vw

1 0 l	$I_{calc.}$	$I_{obs.}$	3 0 l	$I_{calc.}$	$I_{obs.}$
1	52	vst	1	69	m
3	7.0	w	3	8.0	—
5	17	m-	5	18	m+
7	470	vst	7	470	—
9	2.0	—	9	3.0	vw
11	23	w	11	22	vw
13	46	w	13	45	—
15	120	w	15	130	—
17	23	—	17	21	—
19	98	m	19	93	vw
21	320	st	21	320	w
23	36	m	23	36	vw
25	52	m	25	53	w
27	0.6	—	27	0.8	—
29	270	st	29	270	st
31	19	w	31	19	—
33	110	st			
35	140	st			
37	53	m			
39	75	st			
41	44	m			

B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

Table 2 (cont.)

First Layer

1 1 l	$I_{calc.}$	$I_{obs.}$	3 1 l	$I_{calc.}$	$I_{obs.}$
2	1.0	—	2	1.0	—
4	12	w	4	12	—
6	64	m	6	66	w$^+$
8	220	m$^-$	8	180	w$^+$
10	15	m$^-$	10	14	—
12	57	m$^-$	12	58	—
14	410	m	14	410	m
16	15	—	16	16	—
18	41	w	18	40	—
20	20	w	20	19	—
22	220	st	22	220	m
24	2.0	w	24	3.0	—
26	98	st	26	98	m$^+$
28	210	st	28	220	st
30	47	m	30	47	m
32	74	st	32	67	st
34	9.0	w			
36	310	vst			
38	4.0	w			
40	180	vst			

1 0 l	$I_{calc.}$	$I_{obs.}$	2 1 l	$I_{calc.}$	$I_{obs.}$
5	17	w	1	67	m
7	470	vst	3	8.0	—
9	2.0	vvw	5	18	vvw$^+$
11	23	m	7	470	m$^+$
13	46	m	9	2.0	—
15	120	m$^+$	11	23	vvw
17	23	w	13	46	vw
19	98	m$^+$	15	130	vw
21	320	st	17	22	—
23	36	m	19	96	vvw
25	52	m	21	320	m
27	0.6	—	23	35	w
29	270	st	25	50	m
31	19	w	27	0.8	—
33	110	st	29	270	st
35	140	st	31	19	w
37	53	m	33	110	st
39	75	st	35	140	st
41	44	st	37	53	m

508

Table 3

Powder Photographs of $Bi_4Ti_3O_{12}$. Cr K radiation, orthorhombic description

$h\,k\,l$	$10^4 \sin^2\theta_{calc.}$	$10^4 \sin^2\theta_{obs.}$	$I_{obs.}$	$h\,k\,l$	$10^4 \sin^2\theta_{calc.}$	$10^4 \sin^2\theta_{obs.}$	$I_{obs.}$
0 0 8	0779	0771	st	1 1 19	5282 ⎫	5292	m
1 1 1	0903	0895	m	2 2 12	5314 ⎬		
1 1 5	1195	1188	vvw	0 2 18	5710 ⎫	5734	vvw
—	—	1288	m⁻	2 0 18	5735 ⎬		
—	—	1336	w	0 0 22	5887 ⎫	5892	m
1 1 7	1487	1480	vst	1 3 11	5900 ⎬		
—	—	1614	vw	2 2 14	5946 ⎫	5949	m
0 0 12	1752 ⎫	1752	m	3 1 11	5950 ⎬		
0 2 0	1769 ⎬			1 1 21	6255	6267	st
2 0 0	1794	1790	ẇ	0 2 20	6635 ⎫		
0 2 4	1964	1952	vw	2 0 20	6660 ⎬	6664	vw
β0 0 14	1974 ⎫	1974	m⁻	2 2 16	6676 ⎭		
2 0 4	1989 ⎬			0 4 0	7074	7070	vw
0 0 14	2384	2384	vst	1 3 15	7165 ⎫	7172	m
0 2 8	2548 ⎫	2565	st	4 0 0	7174 ⎬		
2 0 8	2573 ⎬			3 1 15	7215 ⎫	7221	m⁻
1 1 13	2947 ⎫	2947	m	4 0 2	7223 ⎬		
β2 2 0	2953 ⎬			1 1 23	7326	7335	w
0 2 10	2985 ⎫	3005	w	2 2 18	7503 ⎫	7511	w
β1 1 15	3003 ⎬			0 4 6	7512 ⎬		
2 0 10	3010 ⎭			0 2 22	7656 ⎫	7674	m
0 0 16	3114	3115	m⁻	2 0 22	7681 ⎬		
0 2 12	3521 ⎫	3538	vvw	0 0 26	8223	8223	w
2 0 12	3546 ⎬			1 1 25	8494	8495	w
2 2 0	3562	3567	m	3 3 7	8611	8611	m
1 1 15	3628	3638	m	2 0 24	8801 ⎫		
0 0 18	3941	3942	w	1 3 19	8819 ⎬	8806	vw
2 2 6	4000	4006	w	0 4 12	8826 ⎭		
0 2 14	4153 ⎫			2 4 0	8868 ⎫	8859	w
β1 3 7	4159 ⎬	4171	st	3 1 19	8869 ⎬		
2 0 14	4178 ⎭			2 4 2	8917 ⎫		
β3 1 7	4200 ⎭			4 0 12	8926 ⎬	8934	vw
2 2 8	4341	4333	w	4 2 0	8943 ⎭		
1 1 17	4406	4418	vvw	2 2 22	9449 ⎫	9458	st
1 3 1	4440	4428	vvw	0 4 14	9458 ⎬		
3 1 1	4482	4490	vvw	0 0 28	9537 ⎫	9551	m
0 0 20	4866 ⎫	4880	w	4 0 14	9558 ⎬		
0 2 16	4883 ⎬			2 4 8	9647	9652	vw
2 0 16	4908 ⎫	4923	w	4 2 8	9722	9714	vw
β2 2 14	4922 ⎬			1 3 21	9792	9785	w
1 3 7	5024	5029	m				
3 1 7	5074	5078	m				

The positions of the Ti atoms are assumed to be:

4 Ti_1 in 4 (a) $0.38 \leq y_1 \leq 0.62$

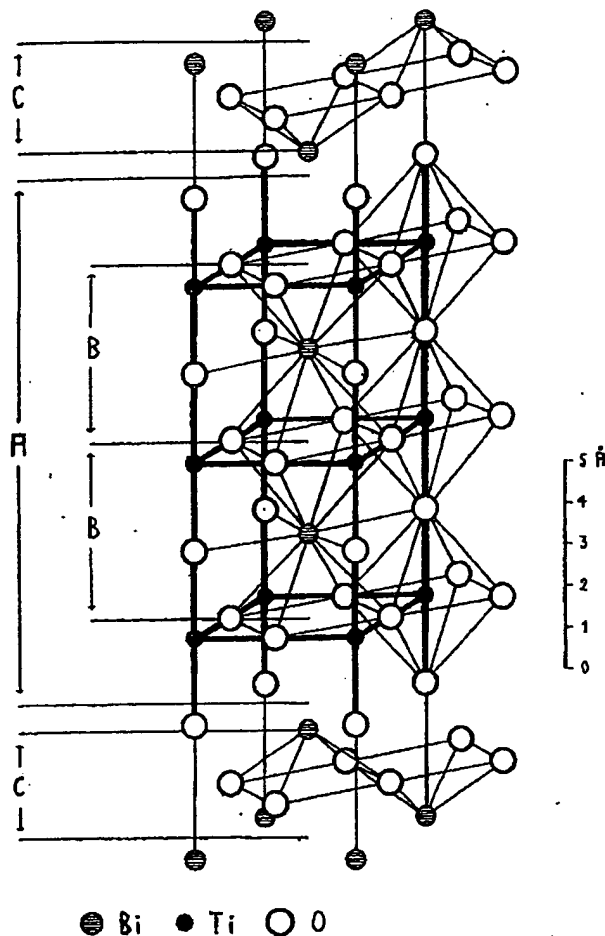8 Ti_2 in 8 (c) $0.38 \leq y_2 \leq 0.62$ $0.102 \leq z_2 \leq 0.176$

B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

Figure 4.

One half of the pseudo-tetragonal unit cell of $Bi_4Ti_3O_{12}$ (from $z \approx 0.25$ to $z \approx 0.75$). A denotes the perowskitic layer $Bi_2Ti_3O_{10}^{2-}$, C $Bi_2O_2^{2+}$ layers and B unit cells of the hypothetical perowskite structure $BiTiO_3$.

In figures 3 a and 3 b sections of one fourth of the unit cell are made for $x = 0$ and $x = 0.25$. (The projections of the positions of the Bi_1, Bi_2 and Ti atoms are denoted by: white circles, double circles and black circles respectively. The same scale is used as for figure 2). Regions where oxygen atoms might be situated are shown by shaded areas. In figure 3 a the positions of the Ti atoms are assumed to be: $0\,0\,\frac{1}{2}$ and $0\,y\,z;\ 0\,y\,\bar{z}\ y = 0.62\ z = 0.139$ and in figure 3 b, $0\,y\,0\ y = 0.62$ and $\pm\,0\,0\,z\ z = 0.324$.

As in the discussion above it was tried to find positions for the O atoms giving an octahedral arrangement around Ti_1 and Ti_2. Only with O atoms situated in the positions 8 (d) $x \approx \frac{1}{4}\ y \approx y_1 + \frac{1}{4}$ and 8 (c) $y \approx y_1\ z \approx 0.058$ would Ti_1 be surrounded by regular octahedra (see figure 3). It was therefore assumed that these positions are occupied by oxygen atoms. For oxygen atoms in contact with Ti_2, the point positions 8 (c) and 16 (e) are possible. With 8 O situated at 8 (c), every Ti atom is in contact with one oxygen atom; with 16 O in 16 (e), Ti_2 may be in contact with 2 O (e_2) or 4 O ($y \approx y_2 + \frac{1}{4}\ z \approx z_2$) ($e_4$). Bear-

510

ing in mind that the unit cell contains 48 O and assuming 16 O to be situated at 8 (o) + 8 (d) (so as to form an octahedron around Ti_1), the following arrangements giving 6 O around Ti_2 seemed possible:
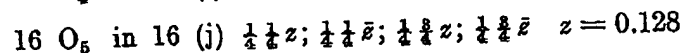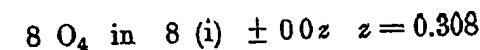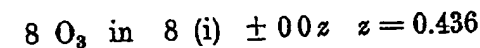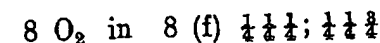
$$\text{a.} \quad 8\ O\ (o)\ +\ 8\ O\ (o)\ +\ 16\ O\ (e_4)$$

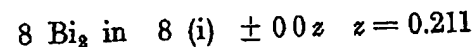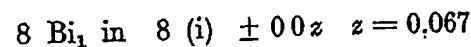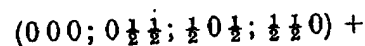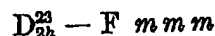$$\text{b.} \quad 16\ O\ (e_2)\ +\ 16\ O\ (e_4).$$
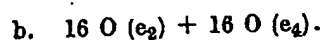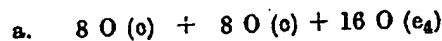
With b. no combination giving octahedra of O around Ti_2 could be found. With a., however, arrangements could be found allowing Ti_2 to be surrounded by an almost regular octahedron. The following parameters for oygen atoms in contact with Ti_1 or Ti_2 were assumed:

$$8\ O_1 \text{ in } 8\ (d) \quad x \approx \tfrac{1}{4} \quad y \approx y_1 + \tfrac{1}{4}$$

$$8\ O_2 \text{ in } 8\ (c) \quad y \approx (y_1 + y_2)/2 \quad z \approx z_2/2$$

$$8\ O_3 \text{ in } 8\ (c) \quad y \approx y_2 \quad z \approx 3 z_2/2$$

$$16\ O_4 \text{ in } 16\ (e) \quad x \approx \tfrac{1}{4} \quad y \approx x_2 + \tfrac{1}{4} \quad z \approx z_2$$
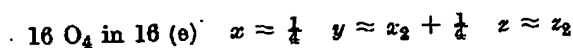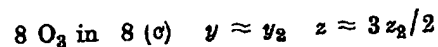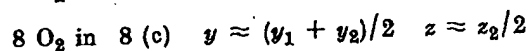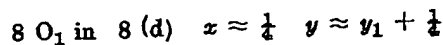
For the remaining 8 O there seemed to be room only in the position 8 (b) $y \approx \tfrac{1}{4}$. It is seen that these positions are basically the same as were arrived at when space group D_2^7 was assumed, except for possible small shifts in the y direction.

Thus no new arrangement was found by assuming C_{2v}^{18} a or b. In Table 2 (pseudo-tetragonal indices) the intensities, calculated by means of the formula $I = (10\ F/4\ f_{Bi})^2$, are compared with the observed ones. Since the ratios f_{Ti}/f_{Bi} and f_0/f_{Bi} vary with $\sin\theta/\lambda$ they were interpolated for every reflection from values taken from the International Tables (3). Table 2 shows good agreement between the calculated and observed intensities.

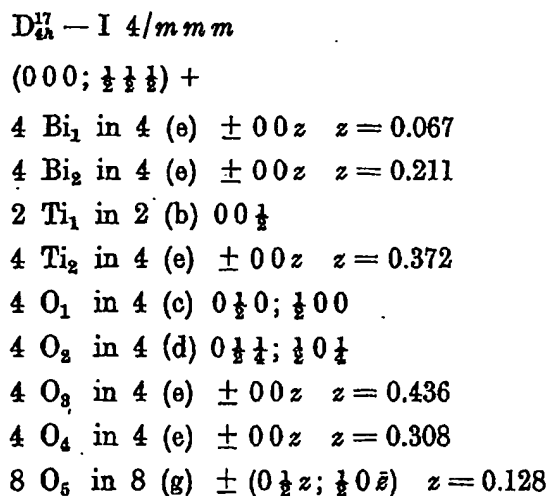The following structure is thus proposed:

$$D_{2h}^{23} - F\ mmm$$

$$(0\,0\,0;\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}0\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}0)\ +$$

$$8\ Bi_1 \text{ in } 8\ (i) \quad \pm 0\,0\,z \quad z = 0.067$$

$$8\ Bi_2 \text{ in } 8\ (i) \quad \pm 0\,0\,z \quad z = 0.211$$

$$4\ Ti_1 \text{ in } 4\ (b) \quad 0\,0\tfrac{1}{2}$$

$$8\ Ti_2 \text{ in } 8\ (i) \quad \pm 0\,0\,z \quad z = 0.372$$

$$8\ O_1 \text{ in } 8\ (e) \quad \tfrac{1}{4}\tfrac{1}{4}0;\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{2}$$

$$8\ O_2 \text{ in } 8\ (f) \quad \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4};\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{3}{4}$$

$$8\ O_3 \text{ in } 8\ (i) \quad \pm 0\,0\,z \quad z = 0.436$$

$$8\ O_4 \text{ in } 8\ (i) \quad \pm 0\,0\,z \quad z = 0.308$$

$$16\ O_5 \text{ in } 16\ (j) \quad \tfrac{1}{4}\tfrac{1}{4}z;\ \tfrac{1}{4}\tfrac{1}{4}\bar{z};\ \tfrac{1}{4}\tfrac{1}{4}z;\ \tfrac{1}{4}\tfrac{1}{4}\bar{z} \quad z = 0.128$$
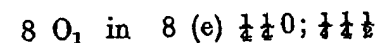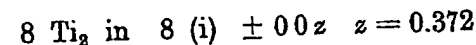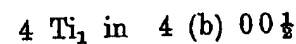
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B. AURIVILLIUS, *Mixed bismuth oxides with layer lattices. II*

For the pseudo-tetragonal cell the positions will be:

$$D_{4h}^{17} - I \; 4/mmm$$

$$(0\,0\,0; \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) +$$

4 Bi_1 in 4 (e) $\pm\,0\,0\,z$ $z = 0.067$

4 Bi_2 in 4 (e) $\pm\,0\,0\,z$ $z = 0.211$

2 Ti_1 in 2 (b) $0\,0\,\tfrac{1}{2}$

4 Ti_2 in 4 (e) $\pm\,0\,0\,z$ $z = 0.372$

4 O_1 in 4 (c) $0\,\tfrac{1}{2}\,0; \tfrac{1}{2}\,0\,0$

4 O_2 in 4 (d) $0\,\tfrac{1}{2}\,\tfrac{1}{4}; \tfrac{1}{2}\,0\,\tfrac{1}{4}$

4 O_3 in 4 (e) $\pm\,0\,0\,z$ $z = 0.436$

4 O_4 in 4 (e) $\pm\,0\,0\,z$ $z = 0.308$

8 O_5 in 8 (g) $\pm\,(0\,\tfrac{1}{2}\,z; \tfrac{1}{2}\,0\,\bar{z})$ $z = 0.128$

In figure 4 one half of the pseudo-tetragonal unit cell is pictured. The structure consists of $Bi_2O_2^{2+}$ layers alternating with $Bi_2Ti_3O_{10}^{2-}$ layers. The arrangements of the atoms within the $Bi_2Ti_3O_{10}^{2-}$ layers seems to be the same as that found for perowskite structures, and it is easily found by calculation that the geometrical properties of the Bi^{3+}, Ti^{4+} and O^{2-} ions make a perowskite structure possible. Thus the structure might be looked upon as a layer structure where perowskitic layers $Bi_2Ti_3O_{10}^{2-}$ — corresponding to a hypothetical perowskite structure $BiTiO_3$ — alternate with $Bi_2O_2^{2+}$ layers. With the notations given by LAGERCRANTZ and SILLÉN (5), the above structure might be denoted by X_{III}.

I wish to thank Professor L. G. SILLÉN for valuable discussions concerning this work.

Stockholms Högskola, Institute of Inorganic and Physical Chemistry, 1949.

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